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REMARKS

This application has been amended in a manner that is believed to place it in condition for allowance at the time of the next Official Action.

Claims 29-31 and 35-49 are pending in the present application. Claims 29 and 31 have been amended to more particularly point out and distinctly claim the present invention. Claims 29 and 49 are the pending independent claims in the present application. Claims 32-34 and 50 have been canceled without prejudice.

In the outstanding Official Action, claim 29 was objected to for reciting the terms "phenoxy ethanol" and "phenoxy propanol" without reciting a comma mark between the two terms. As suggested by the Examiner, a comma mark has been inserted between "phenoxy ethanol" and "phenoxy propanol". Thus, applicants believe that the objection has been obviated.

Claims 33 and 34 were objected to under 37 CFR §1.75(c) as allegedly being of an improper dependent form.

Claims 33 and 34 have been canceled.

Claims 29 and 31-34 were rejected under 35 USC §112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter which applicants regard as the invention. Applicants believe that the present amendment obviates this rejection.

Claim 29 was rejected for reciting the recitation "in an amount less than 25% by weight of solvent". Applicants believe that the Examiner's objection was well taken and has amended claim 29 to recite that the solvent is "in an amount less than 25% by weight of said composition". Support for this recitation may be found in previously pending claim 34.

The outstanding Official Action rejected claims 31-34 for reciting additional solvents. As noted above, claims 32-34 have been canceled. Claim 31 has been amended to recite that the composition further comprises solubility promoters.

Thus, it is believed that claims 29-31 and 35-49 are definite to one of ordinary skill in the art.

Claims 29-50 were rejected under 35 USC §103(a) as being allegedly unpatentable over JP 11-121109 in view of REEVE, DE 19534532, PAULUS et al., RAAD et al., and GRIER et al. This rejection is respectfully traversed.

In imposing the rejection, the Official Action alleged that the JP 11-12109 publication teaches the combination of benzoisothiazolin, mercaptopyridine N-oxide, and hexahydro-1, 3, 5-tris (2-hydroxyethyl)-s-triazine. Moreover, the Official Action alleged that the JP 11-12109 publication taught these ingredients in combination with hydrophilic organic solvents.

However, the Examiner's attention is respectfully directed to independent claim 29. Claim 29 has been amended to recite that the bactericidal N-formal is 3,3'-methylenebis.

Applicants believe that the JP 11-12109 publication fails to disclose or suggest the utilization of 3,3'-methylenebis. Indeed, the JP 11-12109 does not even mention 3,3'-methylenebis. Indeed, a full translation of the publication is attached for the Examiner's convenience.

Moreover, Applicants do not believe that the additional references of REEVE, DE 2337755, DE 19534532, PAULUS et al., RAAD et al., and GRIER et al., alone or in combination with each other, remedy this deficiency.

REEVE is directed to a class of compounds which provide stability of isothiazolones against decomposition. While REEVE discloses that these stabilizers can be used to "lock up" an isothiazolone, REEVE fails to disclose or suggest the bactericidal N-formal of the claimed invention.

As to the DE 2337755 publication, this publication also fails to disclose a bactericidal N-formal that is 3,3'-methylenebis. The DE 2337755 publication is concerned with disinfectants wherein the N-formal is N,N,N-tri(hydroxethyl)-hexahydrotriazine.

The DE 19534532 patent publication teaches an additive mixture. The composition teaches a product containing an n-(cylco)alkyl-isothiazolone, a stabilizer and a solubilizer. However, this publication fails to remedy the deficiencies of the publications noted above.

PAULUS et al. teach a method of preparation and use for 5,5'-dimethyl-di-(1,3-oxazolidin-3-yl) methane. PAULUS et al. also fail to disclose or suggest a composition with the bactericidal of the claimed invention.

RAAD et al. is directed to the control of biofouling in pipes or aqueous systems by using compositions that include a chelator and an antimicrobial agent. The Official Action contends that columns 9-13 of the RAAD et al. patent disclose that chelators improve the activity of antimicrobial compounds such as formaldehyde and isothiazolones. However, while RAAD et al. teach that the chelators may be added to non-oxidizing biocides such as isothiazolones, formaldehyde and glutaraldehyde, RAAD et al. fail to disclose or suggest claimed components or claimed amounts of the present invention.

GRIER et al. is directed to antimicrobials that protect metal-working compositions against fungal and bacterial attack. However, GRIER et al. also fail to disclose or suggest using a composition with the claimed bactericidal. As a result, it is believed that GRIER et al. fails to remedy the deficiencies of the publication noted above.

The Examiner's attention is also respectfully directed to claim 49. Claim 49 recites that the bactericidal N-formal is 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl)tri-ethanol present in a concentration of from 40% to 90% by weight of the

composition. Applicants believe that the proposed combination of publications also fail to render obvious claim 49.

The Examiner's attention is respectfully directed to the JP 11-12109 publication, wherein the publication teaches that a specific ratio must be achieved to obtain the synergistic effect described in the publication. Applicants believe that this precise combination teaches away from the claimed invention. As the publication relies on a precise combination of specific ingredients to obtain a synergistic effect, Applicants believe that one of ordinary skill in the art would lack the motivation and reasonable expectation of success of combining and modifying the teachings of the JP 11-12109 publication with the other references in order to obtain the claimed invention.

Indeed, the REEVE publication also relies on a precise combination of ingredients to obtain its desired effect (see column 3, lines 60-68). Upon reviewing the DE 2337755 abstract, it is also apparent that the composition relies on specific ingredients and amounts to obtain a synergistic effect. Applicants believe that the outstanding Official Action fails to show why one of ordinary skill in the art would disregard these teachings in order to obtain the claimed invention.

Moreover, while these publications disclose individual components of the claimed invention, none of these publications provide the necessary motivation and reasonable expectation of success of combining the components as set forth in the claimed

invention. None of the publications suggest the claimed combination of components or their corresponding amounts.

The Examiner is respectfully reminded that the test for obviousness is not whether each different individually is obvious; rather, it is whether the claimed invention as a whole was obvious at the time the application was filed. *In re Buehler*, 515 F.2d 1134 185 USPQ 781 (CCPA 1975). Thus, while the outstanding Official Action cites to individual components of the claimed invention, applicants view that the outstanding Official Action fails to establish that one of ordinary skill in the art would possess the necessary motivation and expectation of success of combining and modifying the cited publications to obtain the claimed invention.

Claims 29-48 and 50 were rejected under 35 USC 103(a) as allegedly being unpatentable over WO 98/52416 in view of REEVE, DE 2337755, DE 19534532, PAULUS et al., RAAD et al., and GRIER et al. This rejection is respectfully traversed.

In opposing the rejection, the Official Action alleges that the WO 98/52416 publication teaches a composition comprising a biocidal N-formal, 3,3'-methylenebis. However, upon reviewing the WO 98/52416 publication, applicants believe that the publication teaches a preservative that exhibits a synergistic effect when iodopropynylbutyl compounds and formaldehyde compounds are in combination with each other. Indeed, the Examiner's attention is respectfully directed to page 3, lines 7-

15, wherein it is stated that the desired effect of the composition is achieved by the combination of these ingredients.

Indeed, this is demonstrated in Example 2. Example 2 may be summarized as follows:

	N-formal	Isothiazolone	Stabilizer	Solvent/solubility promoters	Stability
Ex. 2, Trial A	MAR™71	-	PYRION-Na	water	Precipitate after 3 weeks at room temperature
Ex. 2, Trial B	-	KATHON™893	PYRION-Na	Water/phenoxy propanol	Precipitate after 4 months at room temperature
Ex. 2, Trial C	MAR™71	KATHON™893	PYRION-Na	Water/propylen eglycol	no precipitation after 4 months

Thus, Example 2 demonstrates that the desired technical effect arises from the combination of the following components:

- MAR™71 (3,3'-methylenebio(5-methyloxazolidine))
- KATHON™893 (2-octyl-2H-isothiazol-3-one), and
- PYRION™Na (2-mercapto pyridine N-oxide).

Thus, the publication teaches that iodopropynylbutyl compounds must be added to the composition.

In light of this precise teaching, applicants believe that one of ordinary skill in the art would lack the motivation that reasonable expectation of success of combining and modifying

the teachings of the 98/52416 publication with the REEVE, DE 2337755, DE 19534532, PAULUS et al., RAAD et al., and GRIER et al. publications to obtain and modify the claimed invention.

Indeed, applicants believe that the outstanding Official Action fails to show the necessary motivation and reasonable expectation of success that one of ordinary skill in the art would need to obtain the claimed invention in view of the cited publications. Thus, applicants believe that the proposed combination of publications fail to render obvious the claimed invention.

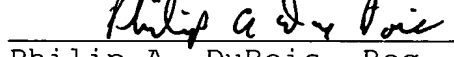
In view of the present amendment and the foregoing remarks, therefore, it is believed that the present application is in now in condition for allowance, with claims 29-31, and 35-49, as presented. Allowance and passage to issue on that basis are accordingly respectfully requested.

The Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any

overpayment to Deposit Account No. 25-0120 for any additional fees required under 37 C.F.R. §1.16 or under 37 C.F.R.§1.17.

Respectfully submitted,

YOUNG & THOMPSON



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APPENDIX:

The Appendix includes the following item(s):

- full translation of JP 11-12109

S 5225

(19) Japan Patent Office (JP) (11) Patent Application Laid Open No.

Hei 11-12109
(12,109/1999)

(43) Laid Open Date: 19 January 1999

(12) Kokai [Laid Open] Patent Gazette (A)

(51) Int. Cl.[6]	Identification symbols	F I
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number of claims: 6 O L [filed online]
examination request: not yet requested (the [Japanese] document totals 8 pages)

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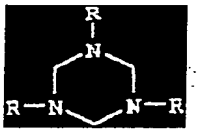
(54) Title of the Invention: Industrial microbicide and industrial microbicidal method

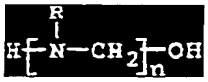
(57) Abstract

[Solution]

To provide an industrial microbicide that characteristically contains 1,2-benzisothiazolin-3-one, sodium 2-pyridinethiol-1-oxide, and N-substituted-N-hydroxymethylamine and polycondensate thereof (including the case of conversion into the cyclic structure



when **n** = 3) with general formula (I)



(I)

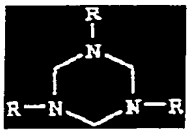
(R is lower alkyl, possibly substituted by the hydroxyl group, and **n** is an integer from 1 to 3) as effective components in proportions at which a synergistic effect appears.

[Advantageous Effects]

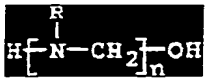
An industrial microbicide can be provided that exhibits a highly persistent, broad-spectrum microbicidal activity at low quantities of addition and that substantially manifests this activity even on disinfection target systems that reside at a basic pH.

Claims

[Claim 1] Industrial microbicide that characteristically contains 1,2-benzisothiazolin-3-one, sodium 2-pyridinethiol-1-oxide, and N-substituted-N-hydroxymethylamine and polycondensate thereof (including the case of conversion into the cyclic structure



when **n** = 3) with general formula (I)



(I)

(R is lower alkyl, possibly substituted by the hydroxyl group, and **n** is an integer from 1 to 3) as effective components in proportions at which a synergistic effect appears.

[Claim 2] The industrial microbicide described in claim 1, wherein the ratio between the 1,2-benzisothiazolin-3-one and sodium 2-pyridinethiol-1-oxide is 1 : 0.1-10 as the weight ratio and the ratio between the total of 1,2-benzisothiazolin-3-one plus sodium 2-pyridinethiol-1-oxide and the N-substituted-N-hydroxymethylamine and polycondensate thereof is 1 : 1-100 as the weight ratio.

[Claim 3] The industrial microbicide described in claim 1 or 2, wherein the N-substituted-N-hydroxymethylamine and polycondensate thereof is 2-hydroxymethylaminoethanol, hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine, or hexahydro-1,3,5-triethyl-s-triazine.

[Claim 4] Industrial microbicidal method, characterized by

adding, by simultaneous or separate addition, industrial microbicide as described in any of claims 1-3 to the disinfection target system so as to provide a total effective component concentration of 10-1,000 mg/liter.

[Claim 5] The industrial microbicidal method described in claim 4, wherein the disinfection target system contains water and has a basic pH.

[Claim 6] The industrial microbicidal method described in claim 4 or 5, wherein the pH of the disinfection target system is at least 9.

Detailed Description of the Invention

[0001]

Field of the Invention

This invention relates to an industrial microbicide and to an industrial microbicidal method. More particularly, this invention relates to an industrial microbicide and an industrial microbicidal method for the purpose of preventing the spoilage and deterioration of industrial products (e.g., metal working lubricants such as cutting lubricants, textile lubricants, paper coating baths such as pigment coating baths, calcium carbonate slurries, paints, latexes, sizes, etc.) by microorganisms such as bacteria, fungi, etc.

[0002]

Description of the Prior Art

Industrial products such as metal working lubricants (cutting lubricants), textile lubricants, paper coating baths (pigment coating baths), calcium carbonate slurries, paints, latexes, sizes, etc., readily support mold growth and are susceptible to spoilage by bacteria and fungi (mold, yeast), and this has led to the use of a variety of industrial microbicides. However, there are few microbicides that are effective against all microorganisms, and it has also been necessary to add the microbicides in large amounts in order for their effects to appear.

[0003]

In the particular case among the aforementioned industrial products of disinfection target systems that contain water and have a basic pH, e.g., metal working lubricants (cutting lubricants), textile lubricants, paper coating baths (pigment coating baths), calcium carbonate slurries, etc., even the isothiazolones and brominated organic compounds heretofore known as industrial preservatives and antifungal agents suffer from the problem of such a prominent

timewise decline in microbicidal activity that a microbicidal activity effective on the long-term cannot be expected (microbicidal activity for at least a month is generally required for these disinfection target systems). Typical examples of the isothiazolones are 5-chloro-2-methylisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, 4,5-dichloro-2-n-octylisothiazolin-3-one, 2-n-octylisothiazolin-3-one, and 1,2-benzisothiazolin-3-one. Typical examples of the brominated organic compounds are 2-bromo-2-nitropropan-1,3-diol, 2,2-dibromo-1-nitroethanol, and 2,2-dibromo-3-nitrilopropionamide.

[0004]
The 1,2-benzisothiazolin-3-one that is an effective component of the present invention is widely known as an active ingredient of non-metal low-toxicity industrial microbicides. However, while it has a strong microbistatic activity, it has a weak microbicidal activity, and it exhibits weak activity against the Pseudomonas species that are a prominent causative microorganism of the microbial contamination of the aforementioned aqueous industrial products. Another problem with this compound is that resistant microorganisms arise in response to its continuous use.

[0005]
The sodium 2-pyridinethiol-1-oxide that is an effective component of the present invention is also known as an industrial microbicide (see Boukin/Boubaizai Jiten [in Japanese; English title: Encyclopedia of Antibacterial and Antifungal Agents], published in 1986 by *Nihon Boukin/Boubai Gakkai* [*The Society for Antibacterial and Antifungal Agents of Japan*]). However, this compound exhibits weak activity against Gram-negative microorganisms, as typified by Pseudomonas species. Moreover, due to its loss of activity in a relatively short period of time, even when used in large amounts it does not always develop a satisfactory microbicidal activity when used by itself.

[0006]
Substituted phenol compounds, and also the N-substituted-N-hydroxymethylamines and polycondensates thereof that are an effective component of the present invention, are known to be industrial preservatives and antifungal agents that are stable in the basic pH region (refer to the aforementioned Boukin/Boubaizai Jiten). However, the N-substituted-N-hydroxy-methylamines and polycondensates thereof exhibit a weak antifungal activity. In addition, the substantial decline in the microbicidal activity of these compounds when they are used at a concentration ≤ the growth-inhibiting concentration of the microorganism has required that their quantity of addition be managed by continually measuring the microbial count.

[0007]
Industrial microbicides are also known that comprise a combination of two members of the above-defined group of compounds that are effective components in the present invention. For example, Japanese Published (Examined or Kokoku or B) Patent Application Number Sho 62-43966 (43,966/1987) describes an industrial microbicide that combines 1,2-benzisothiazolin-3-one and sodium 2-pyridinethiol-1-oxide. A microbicide that combines sodium 2-pyridinethiol-1-oxide and a polycondensate of N-substituted-N-hydroxymethylamine is described in Lubr. Eng., 35(10), 559-63. An algicide that combines 1,2-benzisothiazolin-3-one with N-substituted-N-hydroxymethylamine and polycondensates thereof is disclosed in Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 8-165204 (165,204/1996).

[0008]
These microbicides, based on the synergistic effect of the two components, do exhibit a microbicidal activity superior to that of the single-component microbicides. However, their broad-spectrum microbicidal efficacy has been inadequate, while a persistent microbicidal activity has not been obtained due to the appearance of resistant microorganisms and degradation of the effective component that occur during long-term use.

[0009]

Problems to Be Solved by the Invention

The problem addressed by this invention is to provide an industrial microbicide that exhibits a highly persistent, broad-spectrum microbicidal activity at low quantities of addition and that substantially manifests this activity even in disinfection target systems that reside at a basic pH.

[0010]

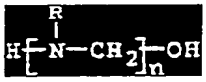
Means Solving the Problems

As a result of research from the perspective described above into combinations of various industrial microbicides, the inventors of the present invention made the surprising discoveries that, through the combination in specific proportions of 1,2-benzisothiazolin-3-one, sodium 2-pyridinethiol-1-oxide, and specific N-substituted-N-hydroxymethylamines and polycondensates thereof, degradation of the 1,2-benzisothiazolin-3-one in the disinfection target system is

inhibited and — in a discovery that could not be predicted from the heretofore known two-component combinations — a substantial microbicidal effect for a variety of microorganisms is developed and is exhibited on a persistent basis. This invention was achieved based on these discoveries.

[0011]
This invention therefore provides an industrial microbicide that characteristically contains 1,2-benzisothiazolin-3-one (BIT), sodium 2-pyridinethiol-1-oxide (NAPT), and N-substituted-N-hydroxymethylamine and polycondensate thereof (including the case of conversion into the cyclic structure given below when **n** = 3) with general formula (I)

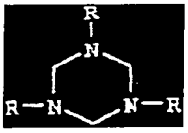
[0012]



(I)

[0013]
(R is lower alkyl, possibly substituted by the hydroxyl group, and **n** is an integer from 1 to 3)

[0014]



[0015]
as effective components in proportions at which a synergistic effect appears.

[0016]
This invention also provides an industrial microbicidal method, characterized by

adding, by simultaneous or separate addition, industrial microbicide as described above to the disinfection target system so as to provide a total effective component concentration of 10-1,000 mg/liter.

[0017]

Embodiments of the Invention

The BIT and NAPT that are effective components in the present invention are both known microbicides, and commercially available BIT and NAPT can be used. General formula (I) represents the N-substituted-N-hydroxymethylamine and polycondensate thereof (including also the case of conversion into the cyclic structure when **n** = 3) that is an effective component in the present invention. The lower alkyl in the substituent R (lower alkyl, possibly substituted by the hydroxyl group) in general formula (I) is C_1 to C_3 alkyl, for example, methyl, ethyl, n-propyl, and isopropyl wherein ethyl is particularly preferred.

[0018]

The N-substituted-N-hydroxymethylamine and polycondensate thereof represented by general formula (I) can be specifically exemplified by 2-hydroxymethylaminoethanol (HMAE), 2,4-bis(2-hydroxyethyl)-2,4-diaza-1-butanol, 2,4,6-tris(2-hydroxyethyl)-2,4,6-triaza-1-hexanol, hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine (HTHT), and hexahydro-1,3,5-triethyl-s-triazine (HTET), among which HMAE, HTHT, and HTET are particularly preferred. Mixtures of two or more of these N-substituted-N-hydroxymethylamines can also be used. Here, polycondensate denotes compounds in which a cyclic structure has been formed accompanying a condensation reaction at **n** = 3 among compounds with general formula (I).

[0019]

Compounds with general formula (I) can be synthesized by known methods; for example, they are readily synthesized from primary amine and paraformaldehyde. As a specific example, HMAE can be synthesized from monoethanolamine and paraformaldehyde (see British Patent 920,301). Commercial products can also be used for compounds with general formula (I), for example, Tomicide G from Yoshitomi Yakuhin Corporation, Bestcide 1087Y and Bestcide 1087T from Dainippon Ink and Chemicals, Incorporated, and Vancide TH from the R. T. Vanderbilt Company. These commercial products are used mainly as preservatives for metal working oils.

[0020]

The proportion between BIT and NAPT in the present invention should be 1 : 0.1-10 as the weight ratio and is preferably 1 : 1-5 as the weight ratio. The proportion between the total of BIT plus NAPT and the N-substituted-N-hydroxymethylamine and polycondensate thereof should be 1 : 1-100 as the weight ratio and is preferably 1 : 5-50 as the weight ratio.

[0021]
The effective components of this invention are preferably used in general formulated as a liquid agent, but the invention is not limited to this and the effective components can be used in powder form depending on the intended application. In addition, when it is desirable to store the effective components separately based on a consideration of long-term formulation storage stability, the individual components can be formulated separately and used in combination at the point of application.

[0022]
When the disinfection target system is, for example, a synthetic resin emulsion, a starch slurry, or an aqueous system such as industrial cooling water or the process water in paper manufacturing, the use of a liquid agent that employs dispersant and water or hydrophilic organic solvent is preferred based on considerations of the solubility and dispersibility of the effective components.

[0023]
The hydrophilic organic solvent can be exemplified by glycols such as ethylene glycol, propylene glycol, diethylene glycol, and dipropylene glycol; glycol ethers such as methyl Cellosolve, phenyl Cellosolve, diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and tripropylene glycol monomethyl ether; alcohols up to C_8; and esters such as methyl acetate, ethyl acetate, 3-methoxybutyl acetate, 2-ethoxymethyl acetate, 2-ethoxyethyl acetate, propylene carbonate, and dimethyl glutarate. These hydrophilic organic solvents are highly qualified for use from the standpoints of safety and stability.

[0024]
The dispersant can be, for example, a cationic surfactant, anionic surfactant, nonionic surfactant, or amphoteric surfactant, wherein nonionic surfactants are preferred from the standpoint of formulation stability. The nonionic surfactant can be exemplified by the ethylene oxide (EO) adducts of higher alcohols, the EO adducts of alkylphenols, the EO adducts of fatty acids, the EO adducts of the fatty acid esters of polyhydric alcohols, the EO adducts of higher alkylamines, the EO adducts of fatty acid amides, the EO adducts of fats and oils, copolymers of EO and propylene oxide (PO), the PO/EO copolymer adducts of alkylamines, fatty acid esters of glycerol, fatty acid esters of pentaerythritol, fatty acid esters of sorbitol and sorbitan, fatty acid esters of sucrose, the alkyl ethers of polyhydric alcohols, and alkylolamides.

[0025]
Water-soluble polymers such as xanthan gum, sodium alginate, polyvinyl alcohol, gelatin, CMC (carboxymethylcellulose), etc., can be used in place of the aforesaid surfactants or as an auxiliary thereto.

[0026]
The following blending proportions are preferably used in the formulation designating 100 weight parts for the formulation: total effective component content = 10-90 weight parts, dispersant = at least 0.01 weight part for each 1 weight part of the total effective component content, water or hydrophilic organic solvent = balance.

[0027]
When the disinfection target system is an oil-based system such as a heavy oil sludge, cutting lubricant, or oil-based paint, the liquid agent is preferably formulated using a hydrocarbon-type solvent such as kerosene, heavy oil, or spindle oil; the aforementioned surfactants can also be added. Furthermore, when the effective components of this invention are formulated divided into 2 or 3 liquids, each effective component can be formulated at the blending proportions given above using the solvents and dispersants described above.

[0028]
For disinfection target systems in which the inventive effective components can be dissolved or dispersed, they may be used directly or as a powder diluted with a solid diluent (for example, kaolin, clay, bentonite, CMC, etc.); the aforementioned surfactants can also be added. In addition, just as for the liquid agent, the effective components can be separately formulated into individual powders. Insofar as the effects are not impaired, formulations according to this invention can include emulsion formulations prepared using water and surfactant and can contain other known microbicides.

[0029]
When in the inventive method the aforementioned effective components are to be added to the disinfection target system simultaneously, it will be convenient to use them as a single formulation as described above. However, they can be used as separate individual formulations when they are to be added separately to the disinfection target system or when it is desirable to have previously kept the individual effective components separated based on considerations of long-term formulation storage stability. The effective components of the industrial microbicide according to this invention are added to the disinfection target system,

either by simultaneous or separate addition, so as to provide a total effective component concentration of 10-1,000 mg/L and preferably 10-500 mg/L.

[0030]
The disinfection target system for the inventive method denotes industrial products such as metal working lubricants (cutting lubricants, rolling lubricants, etc.), textile lubricants, paper coating baths (pigment coating baths), calcium carbonate slurries, synthetic resin emulsions (SBR latexes, etc.), paints (oil-based paints, etc.), adhesives, latex compounds, cement dispersants, sizing agents, etc., and also heavy oil sludges and various aqueous systems such as the process water in paper manufacturing and industrial cooling water.

[0031]
Among the industrial products listed above, the inventive industrial microbicide is preferably applied to industrial products that contain water and are basic (in particular with a pH of at least 9). Preferred disinfection target systems can be exemplified by metal working lubricants (cutting lubricants, rolling lubricants, etc.), textile lubricants, paper coating baths (pigment coating baths), calcium carbonate slurries, and latex compounds, in each case with a pH of at least 9.

[0032]

Examples

This invention is exemplified hereinbelow through formulation examples and test examples, but the scope of the present invention is not limited to these examples. The formulation examples provided below are formulations containing the three effective components of this invention. The comparative formulation examples are formulations that contain one or two of the effective components of this invention. The formulations were prepared by mixing the effective components into the hydrophilic organic solvent and stirring and dissolving to prepare the test agent.

[0033]
The following compounds were used as the effective components in the formulations.

BIT	:	1,2-benzisothiazolin-3-one
NAPT	:	sodium 2-pyridinethiol-1-oxide
HTHT	:	hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine
HMAE	:	2-hydroxymethylaminoethanol
HTET	:	hexahydro-1,3,5-triethyl-s-triazine

[0034]

Formulation Example 1

BIT	2	weight parts
NAPT	8	weight parts
HTHT	10	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Formulation Example 2

BIT	2	weight parts
NAPT	8	weight parts
HMAE	10	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Formulation Example 3

BIT	2	weight parts
NAPT	8	weight parts
HTET	10	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Formulation Example 4

BIT	1	weight part
NAPT	1	weight part
HTHT	50	weight parts
ethylenediamine	1	weight part
water	47	weight parts

[0035]

Formulation Example 5

BIT	15	weight parts
NAPT	3	weight parts
HTHT	40	weight parts
ethylenediamine	15	weight parts
water	27	weight parts

Formulation Example 6

BIT	1	weight part
NAPT	4	weight parts
HMAE	50	weight parts
ethylenediamine	1	weight part
water	44	weight parts

Formulation Example 7

BIT	4	weight parts
NAPT	1	weight part
HMAE	50	weight parts
ethylenediamine	4	weight parts
water	41	weight parts

[0036]

Comparative Formulation Example 1

BIT	2	weight parts
NAPT	18	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Comparative Formulation Example 2

BIT	2	weight parts
HTHT	18	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Comparative Formulation Example 3

NAPT	10	weight parts
HMAE	10	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

[0037]

Comparative Formulation Example 4

HTHT	20	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Comparative Formulation Example 5

HMAE	20	weight parts
diethylene glycol monomethyl ether	50	weight parts
water	30	weight parts

Comparative Formulation Example 6

BIT	2	weight parts
diethylene glycol monomethyl ether	68	weight parts
water	30	weight parts

[0038]

Test Example 1

Test Verifying Microbicidal Activity Using a Pigment Coating Bath

A liquid mixture was prepared from 80 weight parts kaolin, 20 weight parts calcium carbonate, 10 weight parts oxidized starch sizing solution, 5 weight parts SBR latex, 0.2 weight part sodium polyacrylate, and 70 weight parts water. Adjustment of the pH to 9.5 with NaOH gave the pigment coating bath (test material). To this pigment coating bath was then added 1% of a spoiled pigment coating bath (viable count = 5.9×10^7/mL) obtained from a certain paper mill. 500 mg/L or 1,000 mg/L of the test agent prepared in the particular formulation or comparative formulation example was added and the viable count was measured with elapsed time. For the blank, the viable count was measured when no test agent was added. The results are reported in Table 1.

[0039]

Table 1.

test agent	concentration added mg/L	viable count per mL with elapsed time			
		3 hours	1 day	7 days	14 days
Formulation Example 1	500	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
	1000	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
Formulation Example 2	500	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
	1000	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
Formulation Example 3	500	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
	1000	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
Formulation Example 6	500	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
	1000	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
Formulation Example 7	500	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
	1000	$< 10^3$	$< 10^3$	$< 10^3$	$< 10^3$
Comparative Example 1	500	1.9×10^4	5.2×10^5	1.6×10^6	2.5×10^6
	1000	5.0×10^3	9.0×10^3	2.3×10^4	1.7×10^6
Comparative Example 2	500	2.1×10^5	7.5×10^4	6.1×10^5	1.3×10^6
	1000	8.4×10^4	8.0×10^3	2.9×10^4	1.0×10^6
Comparative Example 3	500	6.6×10^4	5.4×10^4	7.3×10^5	1.5×10^6
	1000	1.1×10^4	8.0×10^3	8.1×10^4	9.1×10^5
Comparative Example 4	500	3.0×10^5	8.9×10^4	5.6×10^5	1.2×10^6
	1000	8.5×10^4	1.0×10^4	4.6×10^4	1.1×10^6
Comparative Example 5	500	2.9×10^5	9.1×10^4	5.3×10^5	1.1×10^6
	1000	8.0×10^4	1.2×10^4	4.0×10^4	1.1×10^6
no addition	0	7.3×10^5	1.3×10^6	2.9×10^6	8.2×10^6

[0040]

Test Example 2

Test of Inhibition of Effective Component Degradation Using SBR Latex

The test agent prepared in Formulation Example 1, Comparative Formulation Example 1, Comparative Formulation Example 2, or Comparative Formulation Example 6 was added at 1,000 mg/L to SBR latex (pH = 9.0) obtained from a certain paper mill. The residual BIT concentration was then measured with elapsed time while holding at quiescence at 30°C and the % remaining was calculated. The results are reported in Figure 1. According to the results

in Figure 1, addition of the test agent of Formulation Example 1 resulted in almost 100% of the BIT in the test agent remaining even after 30 days.

[0041]

Test Example 3

Test of Microbicidal Efficacy Against Pseudomonas sp.

Minimum inhibitory concentrations were determined using Pseudomonas sp. isolated from a pigment coating bath from a certain paper mill. The preliminarily cultured bacterial solution was added to a constant amount of liquid bouillon medium, followed by the addition of agent prepared by the addition of HTHT in different proportions to BIT + NAPT ((a) = 1 : 1, (b) = 4 : 1, (c) = 1 : 4). After shake-culture for 24 hours at 37°C, the minimum inhibitory concentration was determined as the concentration at which no increase in optical absorption at 660 nm was observed. The results are reported in Figure 2. The results confirm the appearance of a synergistic effect for the co-use of BIT + NAPT and HTHT.

[0042]

Advantageous Effects of the Invention

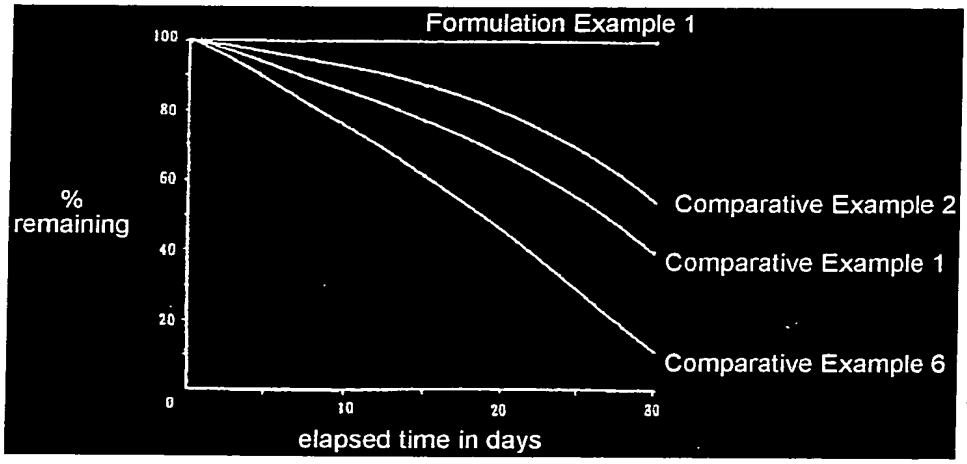
The industrial microbicide according to this invention characteristically contains 1,2-benzisothiazolin-3-one, sodium 2-pyridinethiol-1-oxide, and a specific N-substituted-N-hydroxymethylamine and polycondensate thereof as effective components in proportions at which a synergistic effect appears. As a consequence, compared to the individual effective components used by themselves and to combinations of two of the three effective components, the industrial microbicide according to this invention can manifest microbicidal activity at lower additions against a variety of microorganisms. In addition, since degradation of the effective components in the formulation is inhibited in the inventive industrial microbicide, its microbicidal activity can persist for long periods of time. Its effects are also substantially manifested even in disinfection target systems residing at a basic pH.

Brief Description of the Drawings

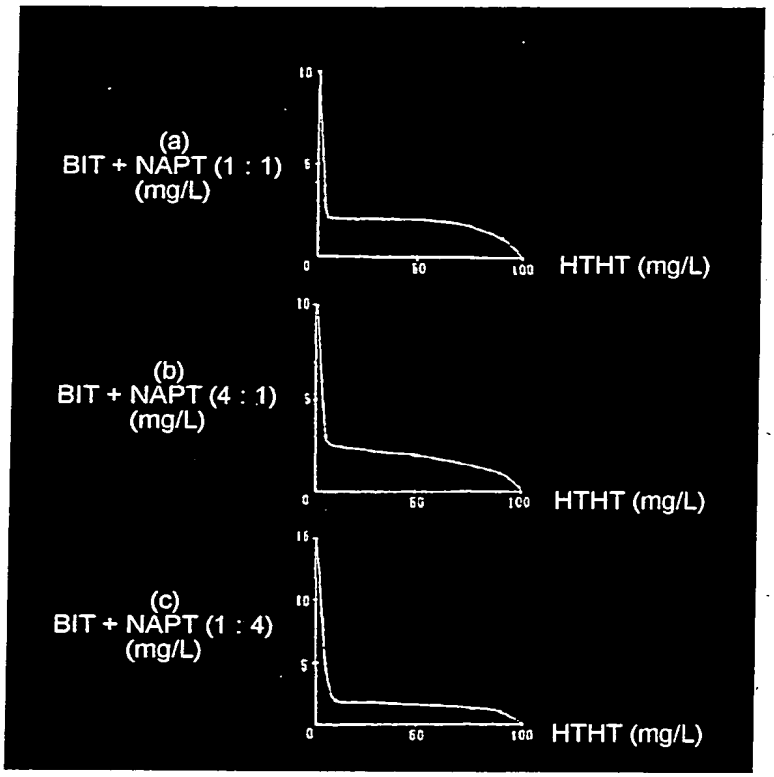
Figure 1 contains a graph that reports the % remaining in the disinfection target system as a function of time for BIT, which is one of the effective components of the industrial microbicide according to the present invention.

Figure 2 contains a graph that reports the minimum inhibitory concentration for the combined use of the HTHT and BIT + NAPT ((a) = 1 : 1, (b) = 4 : 1, (c) = 1 : 4) of the industrial microbicide according to the present invention.

Figure 1.



Figur 2.


(a)
BIT + NAPT (1 : 1)
(mg/L)
HTHT (mg/L)
(b)
BIT + NAPT (4 : 1)
(mg/L)
HTHT (mg/L)
(c)
BIT + NAPT (1 : 4)
(mg/L)
HTHT (mg/L)

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(54) Title: PRESERVATIVE COMPOSITIONS BASED ON IODOPROPYNL- AND FORMALDEHYDE DONOR COMPOUNDS

(57) Abstract

The present invention relates to compositions having broad effectiveness against bacteria and fungi, which comprise (a) an iodopropynylbutyl compound and (b) one or more formaldehyde donor compounds, the formaldehyde donor compounds being N-formals, O-formals and/or a combination thereof. The compositions are also stable and effective in the form of liquid concentrates. The present invention also relates to the use of such compositions in industrial products and to industrial products which comprise these compositions.

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PRESERVATIVE COMPOSITIONS BASED ON IODOPROPYNYL- AND FORMALDEHYDE DONOR COMPOUNDS

The present invention relates to compositions or preservatives for use in industrial products, which protect these products against bacterial and fungal infestation over extended service lives.

Preservatives having a biocidal action for use in industrial products such as cutting fluids, cutting fluids which have been mixed with water, industrial emulsions or other water-based industrial products, and also for household products, such as, for example, cleaning products or cosmetics, such as, for example, bodycare products, are when required generally added to the products to be preserved in low concentration in the form of concentrates.

They protect these products against infestation by bacteria, fungi and yeasts and contribute to long service lives of industrial products, such as, for example, cutting fluids which have been mixed with water, and to a long useful life of household products and cosmetic products.

During their manufacture, storage and their use, preservatives are subject to certain requirements which arise inter alia from the way in which they are added to the abovementioned products in the form of liquid concentrates.

A known fungicidal active ingredient which is frequently used today is iodopropynylbutyl carbamate (IPBC), which is marketed, for example, by Troy Chemie as an organic fungicide preparation in the form of a 20% strength solution of the active ingredient in glycols under the trade name Troyshield F20.

In order to achieve a likewise satisfactory bactericidal effect, it is, however, necessary to combine IPBC with other active substances, e.g. formaldehyde donor compounds. Regarding compatibility with IPBC, however, there are problems when used in concentrates containing formaldehyde donor compounds in the form of strongly alkaline bactericides. Thus, for example, Troy Chemie's technical instruction sheet for Troyshield F20 ™ advises against mixing it with strongly alkaline bactericides, such as, for example, 1,3,5-tris(hydroxyethyl)hexahydrotriazine (Grotan BK ™), because the stability of fungicidally and bactericidally active preparations based on IPBC is impaired.

There has thus been a search for potential ways of improving the stability of IPBC-based compositions for use as preservatives having a fungicidal and bactericidal action.

The prior art includes, for example, an almost white powder consisting of IPBC and a mixture of 1,3-bis(hydroxymethyl)-5,5-dimethylhydantoin and hydroxy-methyl-5,5-

dimethylhydantoin GlydantPlus ™, Lonza AG), which is used as a preservative for cosmetic preparations.

US-A-5,496,842 and US-A-5,428,050 disclose water-soluble compositions comprising a combination of iodopropynylbutyl compounds and N-methylol compounds. It is disclosed that compositions comprising IPBC and N-methylol compounds in a weight ratio of from 1:100 to 1:2000 are in the form of a concentrate powder which, as a water-soluble additive, can be added to industrial products, in particular bodycare products, which then include from 0.01% to 2% of these compositions. The N-methylol compounds mentioned in US-A-5,496,842 and US-A-5,428,050 do, however, include compounds which are not compatible with IPBC, for example 1,3,5-tris(hydroxyethyl)-hexa-hydrotriazine.

EP 0327220 B1 discloses a combination of an iodopropynyl compound with known formaldehyde donors. The disclosed compositions include, as preferred iodopropynyl compound, IPBC and, as formaldehyde donors, non-toxic and odorless compounds which are suitable for use in bodycare products, for example urea derivatives and dimethyloldimethylhydantoin. The compositions of EP 0327200 B1 are likewise added, for example, in the form of solid, water-soluble mixtures, to the products to be preserved.

The known pulverulent concentrates do, however, have a number of technical disadvantages, such as, for example, a tendency toward clumping, a relatively low dissolution rate, a tendency to form dust and the like.

Moreover, the use of odourless, i.e. usually nonvolatile, formaldehyde donors does not, in the case of certain applications, offer adequate antimicrobial protection in the gaseous phase, since no vapour phase of volatile, formaldehyde compounds is present.

In addition, the N-methylols in the form of liquid concentrates mentioned in US-A-5,496,842 and US-A-5,428,050 are not compatible with IPBC, i.e. are unstable and are thus also insufficiently stable in liquid products, such as cutting fluids, which are to be preserved. This is therefore a disadvantage particularly because in industrial products such as cutting fluid emulsions, desired pH stabilization and buffering is achieved inter alia by adding basic, tertiary amines.

The object of the present invention is to provide compositions which protect industrial products against bacterial attack and fungal infestation over extended service lives. The novel compositions should themselves be sufficiently stable and should not decompose under various conditions. In addition, they should be easy to handle and have advantageous technical properties and be easily incorporated into industrial products.

Another object of the present invention is to provide biocidal compositions which include iodopropynylbutyl compounds and formaldehyde donor compounds which are compatible therewith. It should be possible to meter these compositions into standard commercial industrial products, for example by adding a liquid preparation.

Another aim of the present invention is to provide compositions which have improved vapour phase effectiveness compared with the prior art and are sufficiently stable over a wide pH range.

A further object of the present invention is to provide industrial products, such as, for example, cutting fluids, which are distinguished from the prior art by increased stability and improved effectiveness.

This object is achieved by a composition which includes (a) an iodopropynylbutyl compound selected from iodopropynylbutyl esters, ethers, acetals, carbamates and carbonates and (b) one or more formaldehyde donor compounds, and is characterized in that the formaldehyde donor compounds are N-formals formed by the reaction or condensation of a monovalent or polyvalent, amino-substituted C_1-C_{10}-alkyl, -aryl or -aralkyl alcohol and a formaldehyde-supplying compound, and/or O-formals formed by the reaction of a monovalent or polyvalent C_1-C_{10}-alkyl, -aryl -aralkyl alcohol or of a glycol or glycol ether and a formaldehyde-supplying compound, and/or a combination thereof.

Preferred embodiments are the subject-matter of the dependent claims.

The novel preparations preferably comprise iodopropynylbutyl carbamate (IPBC), and the formaldehyde donor compound is preferably an N-formal selected from 3,3'-methylenebis(5-methyloxazolidine) (Mar 71 ™), 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) and 1-aza-5-ethyl-3,7-dioxabicyclo-(3,3,0)octane, particularly preferably a combination of 3,3'-methylenebis(5-methyloxazolidine) (Mar 71 ™) and IPBC.

The compositions comprising the novel iodopropynylbutyl compound and N-formals include the components in amounts, based on the composition, of from 0.1 to 20% by weight of iodopropynylbutyl compound and from 99.9 to 80% by weight of N-formal, preferably from 1 to 10% by weight of iodopropynylbutyl compound and from 99 to 90% by weight of N-formal. The composition particularly preferably comprises from 4 to 6% by weight of iodopropynylbutyl compound, in particular iodopropynylbutyl carbamate, and from 96 to 94% by weight of N-formal, in particular 3,3'-methylenebis(5-methyloxazolidine).

In addition or alternatively to the N-formals according to the invention, the novel compositions may also comprise O-formals formed by the reaction or condensation of formaldehyde-supplying compounds and mono- or polyvalent C_1-C_{10}-alkyl, -aryl or -alkaryl alcohols or glycols or glycol ethers, such as, for example, 1,2-propylene glycol hemiformal, ethylene glycol mono- and/or bisformal, butyldiglycol hemiformal, butylglycol hemiformal, benzyl glycol hemiformal, dipropylene glycol hemiformal and the like.

The compositions comprising the iodopropynylbutyl compound according to the invention and O-formals include the components in amounts, based on the composition, of from 0.1 to 20% by weight of iodopropynylbutyl compound and from 99.9 to 80% by

weight of O-formal, preferably from 1 to 10% by weight of iodopropynylbutyl compound and from 99 to 90% by weight of O-formal. The composition particularly preferably comprises from 4 to 6% by weight of iodopropynylbutyl compound, in particular iodopropynylbutyl carbamate and from 96 to 94% by weight of O-formal, in particular from 96 to 94% by weight of 1,2-propylene glycol hemiformal.

Particularly suitable compositions are also those which comprise from 0.1 to 20% by weight, of an iodopropynylbutyl compound and from 99.9 to 80% by weight of a mixture of N- and O-formals, the weight ratio of N- to O-formals being from 10:1 to 1:10, preferably from 9:1 to 8:2 and particularly preferably from 2:1 to 1:2. These compositions preferably comprise from 1 to 10% by weight of iodopropynylbutyl compound and from 99 to 90% by weight of the mixture of N- and O-formals. Such a composition particularly preferably comprises from 4 to 6% by weight of iodopropynylbutyl compound, in particular iodopropynylbutyl carbamate, and from 96 to 94% by weight of the mixture of N- and O-formals, in particular from 96 to 94% by weight of a mixture of 3,3'-methylenebis(5-methyloxazolidine) and 1,2-propylene glycol hemiformal.

The novel compositions are preferably in stable liquid, viscous liquid or paste form, so that they are easy to handle and can be added easily to an industrial product at any time in order to preserve it.

In addition to the biocidally effective components, the novel compositions may comprise further additives and/or auxiliaries, such as emission-reducing additives, viscosity-modifying additives, wetting agents and solvents which have a favourable effect on the technical properties of the compositions, such as, for example, solubility in water, in total amounts of less than 90% by weight, preferably of less than 30% by weight and particularly preferably of less than 15% by weight. Here, the mixing ratios of the individual additives to one another are in the customary ranges known for biocidal compositions.

Particularly suitable compositions are those which comprise a solvent which is selected from 1,2-propylene glycol, 1-methoxy-2-propanol, phenoxypropanol and phenoxyethanol.

For example, the addition of certain glycols, preferably 1,2-propylene glycol, in amounts of from 1 to 20% by weight, based on the composition, has a positive influence on the odour of the compositions and reduces the emission of readily volatile substances, such as, for example, formaldehyde.

Particularly suitable compositions are those which, based on the composition, include the following components:

a) from 0.1 to 20% by weight, preferably from 1 to 10% by weight and particularly preferably from 4 to 6% by weight, of an iodopropynyl compound according to the invention and

b) from 99.8 to 80% by weight, preferably from 99 to 90% by weight and particularly preferably from 96 to 94% by weight, of a mixture of solvents and N-formals according to the invention or of a mixture of solvents and O-formals according to the invention or of a mixture of a combination of N- and O-formals and solvents and also other additives as described above, the weight ratio of formal to a solvent being from 50:1 to 1:10 and preferably greater than 9:1.

As well as the described additives and solvents, which contribute to improving the properties of the novel compositions, the latter may comprise further known biocidal active ingredients, such as, for example, isothiazolones or mercaptopyridines, of which N-octylisothiazolone (Kathon 893 ™) and 2-mercaptopyridine N-oxide, in particular in the form of its 40% strength aqueous sodium salt solution (Pyrion-Na ™), are particularly preferred ;

The composition may also comprises further additives which improve its stability.

In a specific embodiment of the present invention, the composition, as described above? comprises between 1 % and 10 % by weight of IPBC, between 85 % and 98,5 % by weight of 3-3'-methylene bis (5-methyloxazolidine) and between 0,5 % and 5 % by weight of a stabilizer selected from triethanolamine, pyriondisulfide, sodium sulfate or aluminium oxide.

The novel compositions are in the form of a stable liquid concentrate, a stable working solution prepared by diluting the concentrate, a stable emulsion or a stable suspension. The composition can thus be metered easily and also has a good shelf life and does not decompose under practical conditions. The good handling properties of the composition, compared with the storage, preparation and metering in of active ingredients present in two-component systems, are advantageous.

In particular, the novel composition is in the form of a concentrate, in which case the following requirements placed on concentrates are satisfied:

- broad effectiveness (e.g. against bacteria, yeasts and fungi)
- storage stability, transportation stability and thermal stability
- relative insensitivity towards heat and light
- compatibility with packing materials
- adequate solubility in water and homogeneous distribution properties to achieve problem-free incorporation in the products to be preserved (e.g. aqueous solutions or hydrous products)
- good incorporation into anhydrous or low-water products
- vapour phase effectiveness
- adequate pH compatibility, in particular up to pH 11
- sufficiently low viscosity to enable simple metering.

The novel compositions may effectively be added to industrial products containing industrial preservatives, in particular container preservatives, fuel additives, cutting fluid preservatives, preservatives for cutting fluids which have been mixed with water, emulsions and dispersions in the coatings industry or in metalworking, household products, cosmetics and the like, so that the stability thereof and the service life of the finished products is increased compared with known systems. Increased stability of the novel compositions is particularly apparent from the lower tendency of the active ingredient to decompose, less discoloration and reduced formation of undefined decomposition products.

In addition to the customary constituents, the abovementioned industrial products thus comprise a novel composition whose components are sufficiently compatible both in the concentrate and also in the emulsion or suspension. The industrial products preferably comprise from 1 to 10% by weight, preferably from 2 to 5% by weight and in particular 2% by weight, of the novel composition.

Surprisingly, it has been found that the novel combinations of iodopropynylbutyl compounds and N- and/or O-formals, in particular the combination of iodopropynylbutyl carbamate (IPBC) and 3,3'-methylenebis(5-methyloxazolidine) (Mar 71 ™), have a stability which is significantly improved over the prior art, even if they are present in the form of liquid compositions, such as, for example, solutions or emulsions, in particular liquid concentrates, and are added to the abovementioned industrial products in such a form.

In addition, the effectiveness of the compositions is improved by the addition of further additives as in Patent Claims 15 to 23, and, in particular, it is also possible to improve the effectiveness in the vapour phase.

Moreover, the novel compositions are adequately stable over sufficiently broad pH ranges which are relevant when the compositions are used in industrial products. Their stability is adequate in the pH range up to 12, in particular in the range up to pH 11, especially up to pH 9.

The improvements achieved in the compositions as regards stability, effectiveness and other technically relevant properties, such as pH stability and emission behaviour, are illustrated by the examples below.

Examples

The following abbreviations are used in the examples below:

IPBC	= iodopropynylbutyl carbamate
Mar 71 ™	= 3,3'-methylenebis(5-methyloxazolidine)
Grotan BK ™	= 1,3,5-tris(hydroxyethyl)hexahydrotriazine

BDG = butyldiglycol
POE = phenoxyethanol
DPG = dipropylene glycol
PM = 1-methoxy-2-propanol
PP = phenoxypropanol
Kathon 893 ™ = 45% strength N-octylisothiazolone solution in 1,2-propylene glycol
PE = polyethylene
PLG = propyleneglycol
Preventol D2 ™ = benzyl alcohol hemiformal

Example 1

Compositions of IPBC and Mar 71 ™ with and without 1,2-propylene glycol as solvent

In a test series, compositions based on (90-x)% by weight of Mar 71 + x % by weight of IPBC + 10% by weight of 1,2-PLG were prepared. The IPBC-containing mixtures were slightly cloudy and had to be filtered to give clear, colourless to pale yellow solutions, which were stored at a temperature of +40°C in clear glass in order to test the stability of the compositions.

Table I shows the development, determined by means of HPLC, of the IPBC concentration of the solutions with time over a period of 3 months. Investigations were carried out on solutions having an IPBC starting content of from 0 to 10% by weight.

Table I

IPBC contents: [% by wt.]		1	3	5	10
After 1 month at + 40°C		0.76	2.35	3.83	7.40
After 2 months at + 40°C	-	0.62	1.88	3.04	5.66
After 3 months at + 40°C	0	0.52	1.53	2.49	4.50
	-				

In a second test series, compositions based on (100-x) % by weight of Mar 71 ™ + x % by weight of IPBC without the addition of 1,2-PLG were prepared. The IPBC-containing mixtures were likewise slightly cloudy and were therefore filtered to obtain colourless to pale yellow solutions. These solutions were stored in clear glass at a temperature of +40°C over three months. The development with time of the IPBC contents, determined by means of HPLC, is given in Table II for IPBC starting contents of from 0 to 10% by weight. The stability of the compositions in the absence of 1,2-PLG is negligibly

greater, although in both cases the stability of the compositions is adequate over a sufficiently long storage period.

Furthermore, the formaldehyde emission was measured using a Dräger tube after storage for about three months at a temperature of +40°C. The formaldehyde emission was determined using Dräger tubes 67 33 081 in accordance with Dräger instructions for use no. 234-33081 (Drägerwerk AG, Germany), which involved in each case carrying out 10 strokes at 21°C over a 50 ml wide-necked glass containing 5 g of the sample to be investigated. It was found that the formaldehyde emission increases with increasing IPBC content, as the results in the last line of Table II show. The biocidal effectiveness of the compositions in the gas phase thus also increases with increasing IPBC content in an advantageous manner.

Table II

IPBC contents: [% by wt.)	0	1	3	5	10
After 1 month at + 40°C	-	0.75	2.17	3.71	7.08
After 2 months at + 40°C	-	0.64	1.85	3.06	5.63
After 3 months at + 40°C	-	0.58	1.68	2.69	4.87
Formaldehyde emission [ppm]	3	5	6-7	7	8

Example 2

Compositions of IPBC and various N-formals

The stability and compatibility of IPBC in compositions containing 3% by weight of IPBC, from 80 to 97% by weight of N-formals and 17% by weight of 1,2-PLG were determined as a function of the storage time after the solutions had been stored at a temperature of +40°C in clear glass. A summary of the various percentages in the compositions is given in Table III.

The initially clear, colourless to slightly yellowish solutions became discoloured to varying degrees after storage for three months at a temperature of +40°C. Only the compositions based on IPBC and Mar 71 retained their clear, slightly yellowish appearance.

In all samples, the odour was characteristic, in some cases being pungent from the formaldehyde, and in others being amine-like. Composition F had a considerably weaker odour than composition E, which had a characteristic pungent formaldehyde odour.

Table III

Composition in % by wt.	A	B	C	D	E	F	G	H
Grotan BK ™	97	80						
Isopropanolamine-Grotan BK with amine-excess			97	80				
Mar 71 ™					97	80		
Mar 71 ™ variant with amine excess, not dewatered							97	80
IPBC	3	3	3	3	3	3	3	3
1,2-PLG	-	17	-	17	-	17	-	17
Colour after 3 months at +40°C	A and B; clear red-brown C and D: clear, red E and F: clear, yellowish G and H: clear, red							

A summary of the development of the IPBC content, determined by means of HPLC (IPBC starting content 3% by weight) in the compositions investigated as a function of the storage period, is given in Table IV.

Table IV

IPBC Contents [% by wt.]	A	B	C	D	E	F	G	H
After 1 month	<0.03	0.03	<0.03	<0.03	2.44	2.27	0.73	0.94
After 2 months	<0.03				2.04	1.78	0.53	0.72
After 3,5 months					1.61	1.34	<0.01	0.04

It is found that IPBC is compatible with different N-formals to varying degrees. Incompatibility is apparent in particular from a relatively high degree of discoloration following storage and a relatively high degree of IPBC degradation. Thus, for example, the

low-odour Grotan BK TM is incompatible with IPBC. In contrast, preparations based on IPBC and Mar 71 TM with or without 1,2-PLG are significantly more stable and, after storage for three months at +40°C display on IPBC degradation of only about 50%. The formaldehyde emission increases with increasing IPBC content. The addition of 1,2-PLG to compositions which comprise Mar 71 and IPBC is therefore unfavourable for the stability, but has an advantageous effect on the odour of the compositions.

Example 3

Stability of IPBC and Mar 71 in various solvents

The dependence of the IPBC stability in compositions of IPBC and Mar 71 ™ on various solvents used was tested by storing the compositions in clear glass at a temperature of +40°C. Investigations were carried out on preparations containing 1 or 3% by weight of IPBC combined with 89 or 87% by weight of Mar 71 ™ respectively and in each case 10% by weight of a solvent. The results are given in Tables V and VI.

Table V

Composition [% by wt.]	A	C	E	G	I	K
Mar 71	89	89	89	89	89	89
IPBC	1	1	1	1	1	1
1,2-PLG	10	-	-	-	-	-
DPG	-	10	-	-	-	-
BDG	-	-	10	-	-	-
PM	-	-	-	10	-	-
POE	-	-	-	-	10	-
PP	-	-	-	-	-	10
IPBC Content [% by wt.]						
After 1 month at +40°C	0.74	0.75	0.74	0.77	0.76	0.75
After 2 months at +40°C	0.63	0.66	0.61	0.62	0.57	0.68
After 3 months at +40°C	0.56	0.57	0.54	0.60	0.60	0.60
Formaldehyde emission* (in ppm)	4	5	3	2	5	5

* = measured as described in Example 1 using Dräger tubes (10 strokes) at 21°C after storage for about 3 months at +40°C on 5 g in each case in a 50 ml wide-necked glass.

Table VI

Composition [% by wt.]	B	D	F	H	J	L
Mar 71	87	87	87	87	87	87
IPBC	3	3	3	3	3	3
1,2-PLG	10	-	-	-	-	-
DPG	-	10	-	-	-	-
BDG	-	-	10	-	-	-
PM	-	-	-	10	-	-
POE	-	-	-	-	10	-
PP	-	-	-	-	-	10
IPBC Content [% by wt.]						
After 1 month at +40°C	2.12	2.20	2.15	2.21	2.21	2.17
After 2 months at +40°C	1.72	1.75	1.89	1.90	1.84	1.77
After 3 months at +40°C	1.50	1.57	1.47	1.57	1.52	1.57
Formaldehyde emission* (in ppm)	5	6	6-7	4	6	8

* = measured as described in Example 1 using Dräger tubes (10 strokes) at 21°C after storage for about 3 months at +40°C on 5 g in each case in a 50 ml wide-necked glass.

It has been found that the IPBC content of the preparations, determined by means of HPLC, continually decreases throughout the storage time. The effect of the solvent on the IPBC stability in the presence of Mar 71 is not very great. All investigated compositions showed an IPBC degradation of about 50% after storage for 3 months in clear glass at +40°C. In both test series, the greatest IPBC degradation was in butyldiglycol (BDG). In contrast, relatively suitable solvents for the novel compositions are: dipropylene glycol (DPG), 1-methoxy-2-propanol (PM), phenoxypropanols (PP) and phenoxyethanol.

There were clear differences in the formaldehyde emission determination. As Tables V and VI show, a composition containing 1-methoxy-2-propanol performs particularly well. For example, compared with all the other solvents, the formaldehyde emission was reduced by up to about 50% after three months through the addition of 1-methoxy-2-propanol.

Example 4

Stability of IPBC with various formals

The stabiliy of various IPBC compositions was tested in clear glass at temperatures of +25°C and +40°C. Investigations were carried out with preparations containing 10 % by weight of IPBC and 90 % of formals. The results are given in Tables VII and VIII.

Table VII

Composition [% by wt.]	M	N	O
IPBC	10	10	10
Mar 71™	90	-	-
Preventol D2 ™	-	90	-
PLG hemiformal	-	-	90

Table VIII

IPBC loss of weight [% wt.]								
	after 5 weeks		after 5,5 weeks		after 6,5 weeks		after 3 months	
composition	at 25°C	at 40°C	at 25°C	at 40°C	at 25°C	at 40°C	at 25°C	at 40°C
M	-	-	-	-	1,49	19,13	-	-
N	6,4	31,1	-	-	-	-	-	-
O	-	-	26,25	64,90	-	-	58,33	69,79

Example 5

Stability of IPBC compositions containing further additives

Various additives were added to the compositions M and N and the stability of the resulting preparations were investigated as hereabove mentioned in example 7 ; the results are given in tables IX and X.

Table IX

Composition [% by wt.]	M1	M2	M3	M4	N1
IPBC	10	10	10	10	10
Mar 71™	88	88	88	88	-
Preventol D2™	-	-	-	-	88
Triethanolamine	2	-	-	-	2
Pyriondisulfide™	-	2	-	-	-
Anhydrous sodium sulfate	-	-	2	-	-
Aluminium oxide 90™(Merck)	-	-	-	2	-

Table X

IPBC loss of weight [% wt.]				
	after 5 weeks		after 6,5 weeks	
Composition	at 25°C	at 40°C	at 25°C	at 40°C
M	-	-	1,49	19,13
M1	-	-	3,93	22,85
M2	-	-	0,0	15,84
M3	-	-	3,83	22,0
M4	-	-	1,93	13,79
N	6,4	31,1	-	-
N1	2,5	15,8	-	-

Example 6

Odour modification of Mar 71™ by the addition of O-formals

Compositions containing Mar 71™ with and without 1, 2, 5 and 10% by weight of 1,2-propylene glycol hemiformal were stored at room temperature in clear glass. The preparations proved to be sufficiently stable. However, over time a very slightly cloudy sediment formed in the mixtures. The addition of 1,2-propylene glycol hemiformal resulted in a clear positive odour modification of Mar 71™.

Example 7

Compositions based on Mar 71™ containing other biocides

The stability of compositions which, in addition to 83 - x % by weight of Mar 71™, comprise as further biocide 17% by weight of N-octalisothiazolone (i.e. a 45%

strength N-octylisothiazolone solution in 1,2-PLG = Kathon 893), was tested by storage in clear glass at room temperature. As well as Mar 71™ and Kathon 893™, the formulations in some instances comprised 1, 2, 5 and 10% by weight of 1,2-propylene glycol hemiformal. The preparations were found to be stable. In contrast to the compositions without Kathon 893 ™, no cloudy sediment formed here. The addition of 1,2-propylene glycol hemiformal resulted in a clear positive odour modification of Mar 71 ™.

Example 8

Stability of compositions containing IPBC and various N-formals

The stability of a composition containing 3% by weight of IPBC, 80% by weight of Mar 71™ and 17% by weight of 1,2-PLG was determined by storage in polyethylene at room temperature and at +40°C. The composition stored at room temperature was unchanged, i.e. clear and colourless, after 14 months. The IPBC contents of the investigated compositions, determined by means of HPLC, are given in Table VII. The test proves that the combination of Mar 71 ™ + IPBC + 1,2-PLG is sufficiently stable at various temperatures.

Table XI

	RT	+40°C
IPBC content [% by wt] after 1 month	2.63	2.32
IPBC content [% by wt] after 3 months	2.59	1.28
IPBC content [% by wt] after 8 months	2.22	0.59

As well as Mar 71™, the compatibility of IPBC with 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) as a further N-formal was investigated. In addition to IPBC (3% by weight) and the corresponding N-formal (80% by weight), both compositions also additionally comprise 17% by weight of 1,2-propylene glycol. The IPBC content was determined after storage at room temperature after 1, 3 and 11 months. It has been found that a combination of IPBC and 3,3-methylenebis(tetrahydro-2H-1,3-oxazine) is also sufficiently stable. As Table VIII shows, the IPBC content was still 2.09% by weight after storage for 11 months at room temperature, if 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) was used as N-formal.

Table XII

Composition [% by wt.]	C1	D	C2
Mar 71™	80	-	80
3,3'-Methylenebis(tetrahydro-2H-1,3-oxazine	-	80	-
IPBC	3	3	3
1,2-PLG	17	17	17
	-	-	-
IPBC content zero value	-	-	2.92
IPBC content after 1 month at RT	-	-	2.88
IPBC content after 3 months at RT	2.29	2.81	-
IPBC content after 11 months at RT	-	2.09	-

Example 9

Formaldehyde emission of N-formals

As well as characterizing their compatibility and stability with IPBC, the N-formals Mar 71™ and 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) were tested with regard to their formaldehyde emission behaviour and odour.

For this purpose, 1 g of each of the N-formals was left to stand overnight in a 400 ml beaker covered with para-film. On the following day, the formaldehyde content was then measured using Dräger tubes (10 strokes) as described in Example 1.

The formaldehyde content was 15 ppm (2 strokes 3 ppm) in 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) and 25 ppm (2 strokes 5 ppm) in Mar 71™. Preparations of 80% by weight of each N-formal and 20% by weight of 1,2-propylene glycol display a clearly different behaviour. For example, the addition of 1,2-PLG to 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) leads to a reduction in the formaldehyde content to form 1.5 to 2.5 ppm (20 strokes) and the addition to Mar 71™ to a reduction to 10 ppm (5 strokes 5 ppm), the formaldehyde content being determined as described above for pure N-formals. The experiment shows that the addition of propylene glycol significantly reduces the formaldehyde emission of the N-formals according to the invention.

Claims

1. Composition having broad effectiveness against bacteria and fungi, which includes (a) an iodopropynylbutyl compound selected from iodopropynylbutyl esters, ethers, acetals, carbamates and carbonates and (b) one or more formaldehyde donor compounds, characterized in that the formaldehyde donor compounds are N-formals formed by the reaction of a monovalent or polyvalent, amino-substituted C_1-C_{10}-alkyl, -aryl, -aralkyl alcohol and a formaldehyde-supplying compound, and/or O-formals formed by the reaction of a monovalent or polyvalent C_1-C_{10}-alkyl, -aryl or -aralkyl alcohol or of a glycol or glycol ether and a formaldehyde-supplying compound, and/or a combination thereof.

2. Composition according to Claim 1, characterized in that the iodopropynylbutyl compound is iodopropynylbutyl carbamate (IPBC).

3. Composition according to one of the preceding claims, characterized in that the formaldehyde donor compound is selected from 3,3'-methylenebis(5-methyloxazolidine), 3,3'-methylenebis(tetrahydro-2H-1,3-oxazine) and 1-aza-5-ethyl-3,7-dioxabicyclo(3,3,0)-octane.

4. Composition according to one of the preceding claims, characterized in that the formaldehyde donor compound is 3,3'-methylenebis(5-methyloxazolidine).

5. Composition according to one of the preceding claims, characterized in that the O-formals are selected from polyoxymethylene glycols, polyoxymethylene diacetates and polyoxymethylene dimethyl ethers.

6. Composition according to one of the preceding claims, characterized in that the O-formal is formed by the reaction of glycols or glycol ethers, in particular of 1,2-propylene glycol, dipropylene glycol, ethylene glycol, butyl glycol, butyl diglycol or benzyl alcohol, and a formaldehyde-supplying compound.

7. Composition according to one of the preceding claims, characterized in that the iodopropynylbutyl compound is iodopropynylbutyl carbamate and the formaldehyde donor compound is 3,3'-methylenebis(5-methyloxazolidine).

8. Composition according to one of Claims 1 to 4 or 7, characterized in that, based on the composition, it includes the following components:

a) from 0.1 to 20% by weight, more preferably from 1 to 10% by weight and particularly preferably from 4 to 6% by weight, of an iodopropynylbutyl compound and

b) from 99.9 to 80% by weight, more preferably from 99 to 90% by weight and particularly preferably from 96 to 94% by weight, of N-formal.

9. Composition according to Claim 8, characterized in that, based on the composition, it includes the following components:

a) from 4 to 6% by weight of iodopropynylbutyl carbamate and

b) from 96 to 94% by weight of 3,3'-methylenebis(5-methyloxazolidine).

10. Composition according to one of Claims 1, 2, 5 or 6, characterized in that, based on the composition, it includes the following components:

a) from 0.1 to 20% by weight, more preferably from 1 to 10% by weight and particularly preferably from 4 to 6% by weight, of an iodopropynylbutyl compound and

b) from 99.9 to 80% by weight, more preferably from 99 to 90% by weight and particularly preferably from 96 to 94% by weight of O-formal.

11. Composition according to Claim 10, characterized in that, based on the composition, it includes the following components:

a) from 4 to 6% by weight of iodopropynylbutyl carbamate and

b) from 96 to 94% by weight of 1,2-propylene glycol hemiformal

12. Composition according to one of Claims 1 to 7, characterized in that, based on the composition, it includes the following components:

a) from 0.1 to 20% by weight, preferably from 1 to 10% by weight and particularly preferably from 4 to 6% by weight of an iodopropynylbutyl compound and

b) from 99.9 to 80% by weight, preferably from 99 to 90% by weight and particularly preferably from 96 to 94% by weight, of a mixture of N- and O-formals,

the weight ratio of N- to O-formals being from 10:1 to 1:10, more preferably from 9:1 to 8:2 and particularly preferably from 2:1 to 1:2.

13. Composition according to Claim 12, characterized in that, based on the composition, it includes the following components:

a) from 4 to 6% by weight of iodopropynylbutyl carbamate and

b) from 96 to 94% by weight of a mixture of 3,3'-methylenebis(5-methyloxazolidine) and 1,2-propylene glycol hemiformal having a ratio of N- to O-formal as in Claim 12.

14. Composition according to one of the preceding claims, characterized in that it is in stable liquid, viscous liquid or paste form.

15. Composition according to one of the preceding claims, characterized in that it may also comprise additives and/or auxiliaries, preferably emission-reducing additives, viscosity-modifying additives, wetting agents, stabilizers and solvents.

16. Composition according to Claim 15, characterized in that the solvents reduce the emission of formaldehyde or formaldehyde-containing substances.

17. Composition according to Claim 16, characterized in that the solvent is selected from 1,2-propylene glycol, 1-methoxy-2-propanol, phenoxypropanol and phenoxyethanol.

18. Composition according to one of Claims 15 to 17, characterized in that, based on the composition, it includes the following components:

a) from 0.1 to 20% by weight, more preferably from 1 to 10% by weight, of an iodopropynylbutyl compound and

b) from 99.9 to 80% by weight, more preferably from 1 to 10% by weight, of a mixture of N-formals and solvents or of a mixture of O-formals and solvents or of a mixture of a combination of N- and O-formals and solvents as in one of the preceding claims,

the weight ratio of formal to solvent preferably being from 50:1 to 1:10, and in particular greater than 9:1.

19. Composition according to Claim 18, characterized in that based on the composition, it includes the following components:

a) from 4 to 6% by weight of an iodopropynylbutyl compound and

b) from 96 to 94% by weight of a mixture of N-formals and solvents or a mixture of O-formals and solvents or a mixture of a combination of N- and O-formals and solvents as in one of the preceding claims, the ratio of formals to solvents preferably being from 50:1 to 1:10 and in particular greater than 9:1.

20. Composition according to one of the preceding claims, characterized in that it additionally comprises further known biocidal active ingredients.

21. Composition according to Claim 20, characterized in that an additional biocidal active ingredient is an isothiazolone.

22. Composition according to Claim 20, characterized in that the additional biocidal active ingredient is N-octylisothiazolone or 2-mercaptopyridine N-oxide.

23. Composition according to one of claims 15 to 18 which comprises between 1% and 10% by weight of IPBC, between 85 % and 98,5% by weight of 3,3-methylenebis (5-methyl oxazolidine) and between 0,5 % and 5 % by weight of a stabilizer selected from triethanolamine, pyriondisulfide, sodium sulfate or aluminium oxide.

24. Composition according to one of the preceding claims, characterized in that it is in the form of a stable liquid concentrate, a stable working solution prepared by diluting the concentrate, a stable suspension or a stable emulsion.

25. Use of the composition according to one of the preceding claims or a combination of components (a) and (b) of the composition as in one of Claims 1 to 23 as preservatives for industrial products.

26. Use according to Claim 25, characterized in that the industrial products are industrial preservatives, in particular container preservatives, fuel additives, cutting fluid preservatives, preservatives for cutting fluids which have been mixed with water, emulsions and dispersions in the coatings industry or in metal working, household products, cosmetics and the like.

27. Industrial product, characterized in that it contains a biocidally effective amount of the composition as in one of Claims 1 to 24.

28. Industrial product according to Claim 27, characterized in that it includes industrial preservatives, in particular container preservatives, fuel additives, cutting fluid

preservatives, preservatives for cutting fluids which have been mixed with water, emulsions and dispersions in the coatings industry or in metal working, household products, cosmetics and the like.

29. Industrial product according to Claim 27 or 28, characterized in that it preferably comprises from 1 to 10% by weight, preferably from 2 to 5% by weight and in particular 2% by weight of the composition as in Claims 1 to 23.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/00766

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N47/12 //(A01N47/12,61:00,43:90,43:86,43:76,35:02,31:04, 31:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 547 480 A (BAYER AG) 23 June 1993 see page 2, line 1 - line 4 see page 20, line 20 - line 54 see page 3, line 40 - line 42 see page 3, line 58 - page 4, line 1 see page 4, line 3 see page 4, line 12 - line 15	1,2,6, 10,14, 15,24-29
Y	---	3-5,7-9, 11-13, 16-23
Y	EP 0 327 220 A (LONZA AG) 9 August 1989 cited in the application see page 3, line 20 - line 47	3-5,7-9, 11-13, 16-23
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
25 August 1998	07/09/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lamers, W

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INTERNATIONAL SEARCH REPORT

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PCT/IB 98/00766

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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